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1,2-Dimethylimidazolium-functionalized cross-linked alkaline anion exchange membranes for alkaline direct methanol fuel cells

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ABSTRACT

The cross-linked and alkali stable alkaline anion exchange membranes (AAEMs) based on 1,2-dimethylimidazolium (proved to be much more stable than C2-unsubstituted imidazolium cation) were prepared by a hot-pressing method. The properties of these membranes, e.g., water uptake, swelling degree, ion-exchange capacity, conductivity and thermal and chemical stability, were characterized systematically. The swelling degree of the membranes decreases with the decrease of the amount of 1,2-dimethylimidazolium salt, up to 5.8%. The membranes are thermally stable below 200 °C. Alkaline direct methanol fuel cell (ADMFC) fabricated by using CoO_x/C as the cathode catalyst and PtRu/C as the anode catalyst presents a promising performance with the peak power density of 12.7 mW cm⁻² at a current density of 45 mA cm⁻², indicating that the 1,2-dimethylimidazolium-functionalized AAEMs are promising for the application in ADMFCs. Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Recently, alkaline anion exchange membrane fuel cells (AAEMFCs) have been evoked great interests due to the much faster kinetics of fuel electro-oxidation in alkaline environment than that in an acidic media [1–3]. Consequently, noble metals or inexpensive metals/metal oxides can be used as catalysts under alkaline conditions, greatly reducing

the cost of the AAEMFCs. In addition, if using methanol as the fuel, the methanol crossover problem would be highly reduced because of the opposite direction of OH⁻ anion migration to that of the movement of the fuels in the AAEMFCs [2,4,5]. Moreover, the utilization of alkaline anion exchange membranes (AAEMs) replacing the aqueous KOH electrolyte may fundamentally solve the problem in conventional alkaline fuel cells, including the electrolyte leakage and carbonation problem [2].

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However, one of the major challenges associated with the development of AAEMFCs is the availability of suitable alkaline anion exchange membranes (AAEMs) that provide suitable hydroxide conductivity and chemical stability under basic conditions. So far, quaternary ammonium groups are the most commonly used anion exchange groups [1,6–9]. The AAEMs with quaternary ammonium functionality, which have been investigated for many years, exhibit a relatively high ion conductivity (up to 10^{-1} S cm $^{-1}$ at 50 °C [10,11]) due to the efforts of the researchers on modifying the chemical structure of the polymers used to prepare the membranes. However, the quaternary ammonium-based membranes might be unstable in alkaline environment, which makes the membranes unsuitable to be used in the severe alkaline environment. Aiming at enhancing the stability of the AAEMs, many alternative cationic head-groups with high chemical stability in the alkaline condition, such as guanidinium [12,13] and phosphonium [14,15], have been widely discussed. However, the membranes based on these groups are of lower conductivity and high cost, resulting in commercial unavailability. Imidazolium cations, low cost and theoretically stable due to the π -conjugated structure of the five-member heterocyclic ring, have been widely reported [16–20]. Extensive studies have shown that the imidazolium-type AAEMs are relatively stable at 60 °C [16,17,19,21–23]. However, whether the imidazolium-based AAEMs would be suitable for the application in the AAEMFCs and whether the modification on the C2-position would enhance the alkali stability of the imidazolium are worth to be investigated.

In this paper, we prepared imidazolium-based membranes and investigated the possibility of these membranes used for the ADMFCs. First, C2-unsubstituted imidazolium and 1,2-dimethylimidazolium salts (with benzyl) were synthesized and the chemical stability of these imidazolium salts were compared. Then the 1,2-dimethylimidazolium salt, which is more stable, was used to synthesize copolymers with high molecular weight, as well as crosslinkable structure. Finally, the copolymers were hot-pressed to prepare cross-linked membranes. The hydroxide conductivity and dimension stability properties of the membrane were balanced by adjusting the ratio of 1,2-dimethylimidazolium to styrene. The properties of the membranes, such as water uptake, swelling degree, ionic exchange capability (IEC), hydroxide ion conductivity, and chemical stability, were investigated systematically. Finally, the feasibility of the AAEMs was studied in the ADMFCs.

Experimental section

Materials

4-Vinylbenzyl chloride (VBC, 90%), divinyl benzene (DVB), 1-methylimidazole and 1,2-dimethylimidazole were used as purchased. Styrene was distilled under a reduced pressure. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from boiling methanol. Dimethyl sulfoxide (DMSO) was stirred over CaH $_2$ for 24 h, then distilled under reduced pressure and stored over 4 Å molecular sieves under a nitrogen atmosphere. Deionized water was used in the experiments.

Synthesis of 1-methyl-3-(4-vinylbenzyl) imidazolium chloride ([MVBIM][Cl]) and 1, 2-dimethyl-3-(4-vinylbenzyl) imidazolium chloride ([DMVBIM][Cl])

The [MVBIM][Cl] and [DMVBIM][Cl] were synthesized by the nucleophilic substitution reaction of 4-vinylbenzyl chloride with 1-methylimidazole or 1,2-dimethylimidazole via a modified way referred to literature [24]. The procedure is as follows. Anhydrous ethanol, 4-vinylbenzyl chloride and 1-methylimidazole or 1,2-dimethylimidazole were added sequentially to a pre-dried Schlenk tube, then the mixed solution was magnetically stirred under nitrogen atmosphere for 0.5 h, then heated to 60 °C and maintained for 7 h. The solution was added dropwise into ethyl acetate under magnetically stirring at room temperature, then light yellow precipitate was obtained. The precipitate was dried by rotating evaporator at 50 °C and stored in glove box for further used.

The chemical structure and the purity of these imidazolium small molecular compounds were characterized by NMR spectra (Fig. 1). Fig. 1A and B are the ^1H and ^{13}C NMR spectra of [MVBIM][Cl] and [DMVBIM][Cl]. From the ^1H NMR spectrum of [MVBIM][Cl], it can be found that the proton signal (labelled 1 in the molecular structure) belonging to the C2 of imidazole ring disappeared, resulting from the hydrogen/deuterium (H/D) exchange of the proton on the C2 of the imidazolium [MVBIM][Cl] with D $_2$ O, which was testified in literatures [25–29]. From the NMR results, it can be concluded that the C2-unsubstituted imidazolium and 1,2-dimethylimidazolium salts were synthesized successfully and relatively pure.

Synthesis of cross-linked copolymers based on [DMVBIM][Cl]

[DMVBIM][Cl] was dissolved in DMSO under magnetically stirring in nitrogen environment. A certain amount of AIBN (1 mol% double bond), different portions of styrene (the ratio of styrene to [DMVBIM][Cl] is from 1:4 to 5:1) and DVB were added to the [DMVBIM][Cl] solution. After being freeze-thaw degassed twice, the flask was placed in an oil bath thermostated at 70 °C under stirring for 24 h to obtain the product, which was then dried in a vacuum oven at 80 °C overnight.

Membrane preparation

The membranes were cast by a hot-pressing method as follows. The cross-linked copolymers were put between two pieces of insulating films, fixed with two steel plates, then heated to 100–150 °C and pressed at 11 MPa for 1 h. Finally, the three layer films were immersed in water to apart the membranes from the insulating film.

By treating the membranes in 1 M KOH solution at room temperature for two days, the chloride ions were exchanged with hydroxide ions. The membranes were taken out from the alkaline liquor and thoroughly washed with deionized water.

Structure and morphological characterization

The structures of the [MVBIM][Cl] and [DMVBIM][Cl] before and after being treated in 1 M KOH at different temperatures

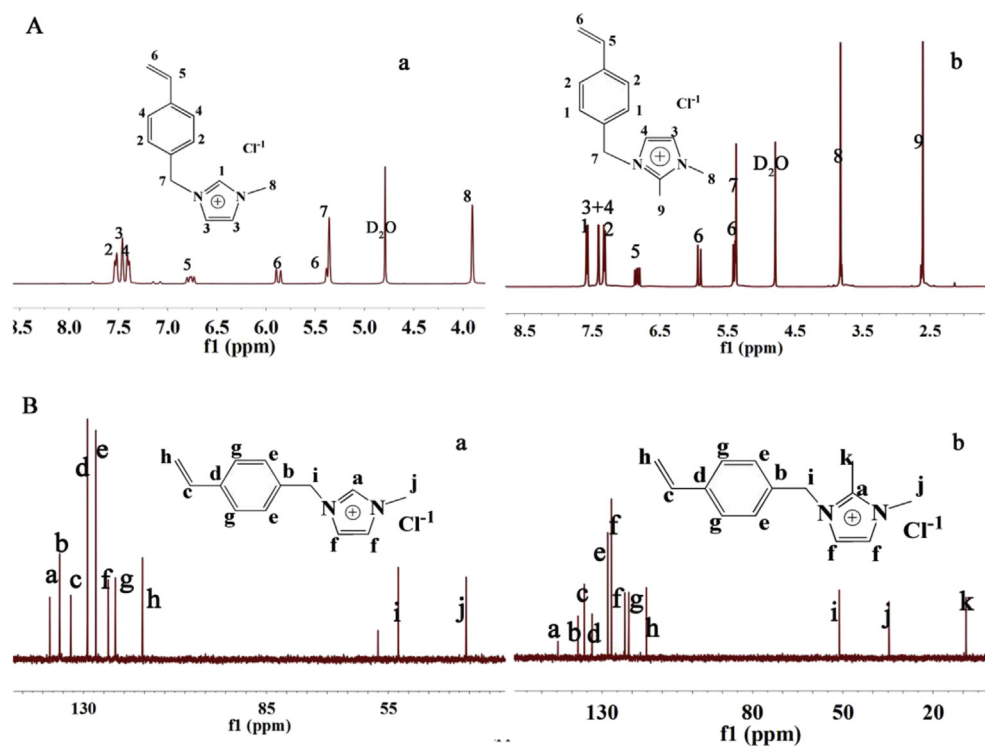


Fig. 1 – ¹H and ¹³C NMR spectra of [MVBIM][Cl] and [DMVBIM][Cl] in D₂O. A is the ¹H NMR spectra of [MVBIM][Cl] and [DMVBIM][Cl]: a) [MVBIM][Cl] and b) [DMVBIM][Cl]; B is ¹³C NMR spectra of [MVBIM][Cl] and [DMVBIM][Cl]: a) [MVBIM][Cl] and b) [DMVBIM][Cl].

were determined by NMR spectra carried out on Bruker ACIII 400 spectrometer in D₂O.

The morphologies of the membranes were characterized by scanning electron microscopy (SEM) with JEOL 6390LV. For observation, the membrane samples were sputtered with gold.

Ion-exchange capacity

Ion-exchange capacity (IEC) of the membranes was determined by the back-titration method. The dried membranes in OH⁻ form were immersed into 40 mL HCl solution for two days, then the potassium hydroxide solution was titrated into the acid solution to determine the IEC.

The calculation of IEC was as follows:

$$IEC(\text{mmol } g^{-1}) = \frac{N_{\text{OHCl}} - N_{\text{IHCl}}}{m}$$

where N_{OHCl} and N_{IHCl} are the moles of HCl before and after the membrane neutralization, and m is the mass of the dried membrane in OH⁻ form.

Water uptake (WU) and swelling degree (SD)

The WU of the membranes in OH⁻ form was calculated from the weight and dimension differences of membranes after soaking in deionized water for 48 h at room temperature and after drying in a vacuum oven. The membranes were soaked in deionized water for 48 h at room temperature and measured after being gently blotted the surface excess water.

To avoid absorbing water in the air, the membranes were measured immediately after being dried for more than 8 h at 80 °C in vacuum.

The WU was calculated by the equation as follows:

$$WU(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100$$

where W_{wet} and W_{dry} are the weight of wet and dry membranes in OH⁻ forms in grams, respectively.

The SD was calculated by the equation as follows:

$$SD(\%) = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100$$

where L_{wet} and L_{dry} are the geometric length of the wet and dry membranes, respectively.

Ionic conductivity

The conductivity was calculated as follows:

$$\sigma = \frac{L}{WTR}$$

where σ is the conductivity of the membrane in S cm⁻¹, L is the length of the membrane between sensor II and reference electrodes in cm, W and T are the width and thickness of the membrane in cm, respectively. R is the resistance of the membrane in ohms. The resistance of the membranes in OH⁻ form were measured in-the-plane (in-plane or parallel) with a Solartron AC impedance spectrometer (1260 impedance

analyser, 1287 electrochemical interface, Zplot software), with the frequency ranging from 1 Hz to 1 MHz. Alternating voltage was applied to the working and counter electrodes with 10 mV amplitude. The resistance was determined from the semi-circle regression of the Nyquist plot and the real resistance was taken as the intercept on X-axis of this regression, while the phase angle was zero degree.

Thermal and chemical stability

The thermal stability of the membranes was investigated by a thermo gravimetric analysis (TGA) in a temperature range from room temperature to 600 °C at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

The chemical stability of the membranes was monitored by measuring the changes of the ionic conductivity of the membrane before and after being kept in 1 M KOH solution at 60 °C for a certain time.

Single cell tests

The catalyst electrodes were 40 wt% PtRu/C (Johnson Matthey) with metal loading of 2 mg cm⁻² as the anode and the homemade CoO_x/C with loading of 2.2 mg cm⁻² as a cathode, respectively. The anode, cathode electrodes and the membranes were directly put together (without hot-pressing) to fabricate the membrane electrode assembly (MEA). The active area of the resulting electrode was 1 cm².

The polarization curves of AAEMFCs were evaluated by a fuel cell test system (FCTS, Arbin Co.). 2 M CH₃OH containing 1 M KOH with the flow rate of 1 mL min⁻¹ was fed to the anode and simultaneously 80 sccm of O₂ was fed to the cathode. The test temperature was 60 °C.

Results and discussion

Stability of the imidazolium cations in alkaline media

The chemical stability of the imidazolium salts was tested in 1 M KOH using NMR spectra to characterize. Fig. 2 shows the ¹H NMR spectra of the [MVBIM][Cl] and [DMVBIM][Cl] before and after being treated in 1 M KOH solution at different

and after being treated in 1 M KOH solution at room temperature and 80 °C. Fig. 2A is for [MVBIM][Cl] and Fig. 2B is for [DMVBIM][Cl]. From Fig. 2A, it can be seen that no new peaks were observed in the ¹H NMR spectra of [MVBIM][Cl] after exposure to 1 M KOH solution at room temperature, indicating that [MVBIM][Cl] was relatively stable in 1 M KOH solution at room temperature. However, two new peaks appeared at about 8.5 and 2.3 ppm in the ¹H NMR spectra after being treated at 80 °C. Correspondingly, a new peak emerged at about 173 ppm in the ¹³C NMR spectra (as shown in Supporting information Fig. S1). From the results of NMR characterization, it can be concluded that [MVBIM][Cl] is unstable in 1 M KOH solution at 80 °C. However, no new peaks are found in the ¹H NMR spectra of [DMVBIM][Cl] after being treated in 1 M KOH (Fig. 2B), indicating that [DMVBIM][Cl] is stable below 80 °C.

The NMR results show that [DMVBIM][Cl] is much more stable than [MVBIM][Cl], indicating that 1,2-dimethylimidazolium has a significant advantage over C2-unsubstituted imidazolium in alkaline environment. Therefore, the cross-linked AAEMs based on 1,2-dimethylimidazolium were further investigated.

Preparation and characterization of cross-linked 1,2-dimethylimidazolium-based membranes

Preparation of cross-linked 1,2-dimethylimidazolium-based membranes

As we know, [DMVBIM][Cl] is hydrophilic with high conductivity, while the styrene is hydrophobic and chemical stable. To obtain copolymers with excellent properties, cross-linked copolymers with different molar ratios of [DMVBIM][Cl] to styrene, including 1:3, 1:4 and 1:4.5, were prepared and discussed extensively. Scheme 1 is the synthetic route for the 1,2-dimethylimidazolium-functionalized cross-linked copolymers. The copolymers were cast into membranes by a hot-pressing method. Accordingly, the membranes are termed as M3, M4 and M4.5, respectively.

Characterization of cross-linked 1,2-dimethylimidazolium-based membranes

Morphological characterization. Visually, the membranes are flexible, transparent, and can be cut into any sizes or be bent

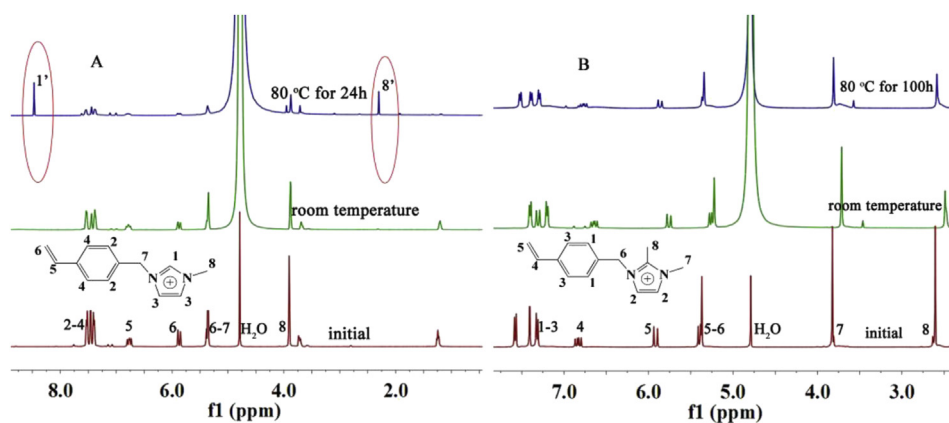
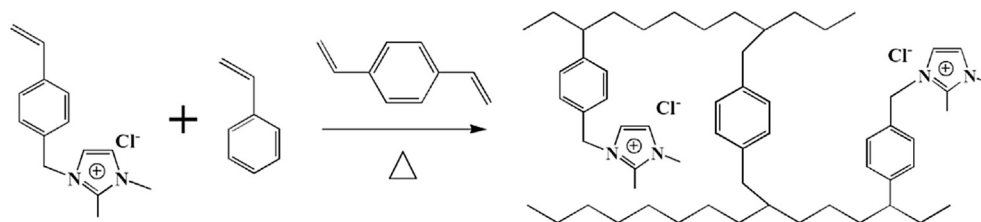


Fig. 2 – ¹H NMR spectra of [MVBIM][Cl] and [DMVBIM][Cl] before and after being treated in 1 M KOH solution at different temperature. A) [MVBIM]⁺; B) [DMVBIM]⁺.



Scheme 1 – Synthetic route for the 1,2-dimethylimidazolium-functionalized cross-linked copolymers.

at any degrees in wet condition. The morphology of the M3 membrane was characterized by SEM as shown in Fig. 3. Fig. 3a and b are the through views of the membranes, while Fig. 3c and d are the plane views of the membrane. It can be seen that the surface of the membrane is relatively smooth and compact without obvious defects or cracks on surface.

IEC, water uptake, and swelling degree. IEC value reflects to a certain extent the properties of the membranes, such as water uptake, swelling degree, and ionic conductivity. As shown in Table 1, the IEC values decrease from 1.33 to 0.95 mmol g⁻¹ with the increase in styrene proportions. Accordingly, the water uptake decreases from 70.4% to 32.9% and the swelling degree from 20.0% to 5.8%. It is deduced that the decreased IEC, WU and swelling degree is due to the increase in hydrophobic groups with the increased proportion of styrene in the membranes.

Especially, the cross-linked membrane-M4.5 shows a swelling ratio of 5.8%, which was much smaller than that of Nafion 117[®] membrane in Na⁺ form (21.7%) and [PMVBIm][OH] membrane [23] with imidazolium as the functional group, indicating that M4.5 is relatively stable in dimensionality.

Ionic conductivity. As shown in Table 2, the conductivities of the membranes increase with the increase of the [DMVBIM][Cl] proportion in the membranes. The conductivities of M3, M4, and M4.5 are 20.8, 11.8, and 10.8 mS cm⁻¹ at 20 °C in deionized water, respectively, which are suitable for hydroxide exchange membrane materials used in fuel cells announced with a prescribed minimum conductivity above 10⁻² S cm⁻¹ [12].

Thermal and chemical stability analysis. TGA curve of M3 is presented in Fig. 4. The slight weight loss (<8%) of M3 below 200 °C is due to the evaporation of water and solvent (DMSO), and the weight loss between 200 and 300 °C is ascribed to the degradation of imidazole groups. A sharp decomposition at about 412 °C is observed, which agrees with that reported in literature [16,30]. The weight loss is due to the decomposition of the phenyl groups, which is the main chain of the membranes. The TGA result indicates that the membranes in OH⁻ form are stable below 200 °C, which can meet the demand of AAEMFCs.

To investigate the chemical stability of the membranes in alkaline, the membranes were immersed in 1 M KOH solution at 60 °C for 200 h Table 3 shows the changes of the

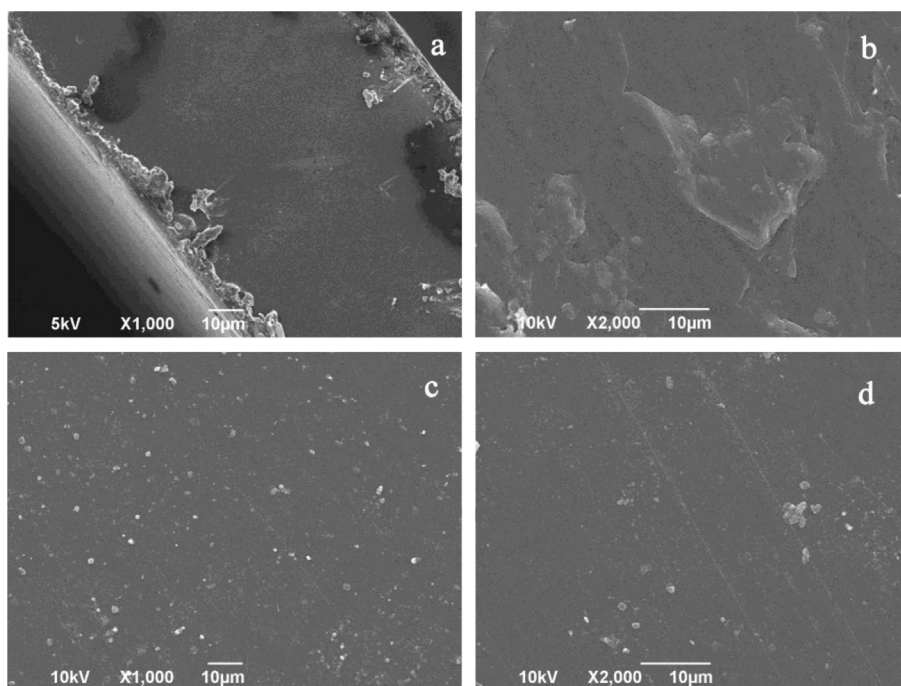


Fig. 3 – SEM images of M3. (a) and (b) through side view; (c) and (d) plane side view.

Table 1 – IEC, WU and swelling degree of the membranes.

	IEC/mmol g ⁻¹	WU/%	SD/%
M3	1.33	70.4	20.0
M4	1.17	45.3	13.8
M4.5	0.95	32.9	5.80
Nafion®117 Na ⁺	–	–	21.7
[PMVBIm][OH] [23]	1.58	86.4	20.8

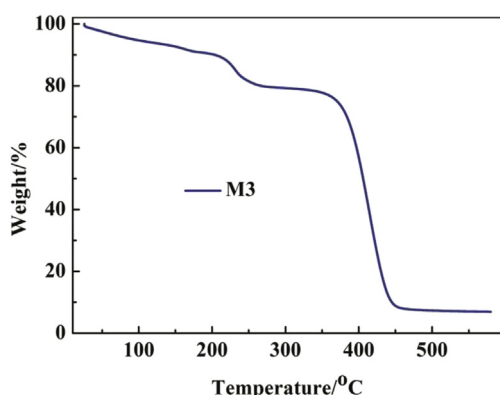
conductivities of the membranes over different immersion times. It is found that the conductivities of the membranes increase at the beginning, then decrease. The conductivities of the membranes increase at the beginning may be due to the replacement of the residue Cl⁻ in the membranes by OH⁻ slowly (the conductivity of Cl⁻ is lower than that of OH⁻). Though the conductivity of the M3 membrane decrease almost to the half, the conductivities of the M4 and M4.5 membranes decrease slightly (<2 mS cm⁻¹), showing that the M4 and M4.5 membranes are relatively stable in 1 M KOH solution at 60 °C for a certain time.

ADMFC single cell tests. The membrane samples of M3 and M4.5 in OH⁻ form are used for MEA fabrication. Fig. 5 shows the polarization curves of the cells. A peak power density of 12.4 mW cm⁻² is obtained at a current density of 45 mA cm⁻² (fuel cell with M3), showing that these 1,2-dimethylimidazolium-based membranes have the potential application in the ADMFCs. The power density (11.3 mW cm⁻²) of the fuel cell with M4.5 membrane is lower than that with M3. The reason may be due to the lower conductivity of M4.5. Considering use of the non-precious metal, CoO_x/C, as the cathode electrocatalyst and absence of any ionomer in the catalyst layer, the relatively lower value of the OCV is acceptable. There is a large space left to improve the fuel cell

Table 2 – Ionic conductivities of the membranes.

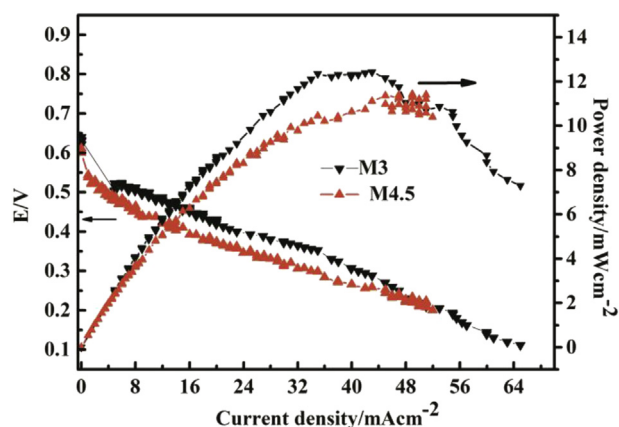
Samples	Conductivity ^a /mS cm ⁻¹
M3	20.8
M4	11.8
M4.5	10.8

^a Measured at 20 °C in DI water.

**Fig. 4 – TGA curves of the M3 membrane.****Table 3 – Changes of the conductivities of the membranes treated in 1 M KOH solution at 60 °C.**

	Conductivity ^a /mS cm ⁻¹				
	0 h	70 h	100 h	120 h	200 h
M3	20.8	27.7	22.1	16.4	10.1
M4	11.8	19.4	14.7	10.9	10.4
M4.5	10.8	18.5	16.5	10.7	9.0

^a Measured at 20 °C in DI water.

**Fig. 5 – Performances of the alkaline direct methanol fuel cells with M3 and M4.5 membranes at 60 °C.**

performance by optimizing the interfacial property between the electrodes and the membrane [31]. Further researches on optimization of the electrode structure and testing conditions are going on in our lab.

From the results of IEC, WU, SD, ionic conductivity, thermal and chemical stability of the membranes and the polarization curves of the fuel cells, it can be seen that the membranes based on 1,2-dimethylimidazolium could meet the requirement of AAEMs in ADMFCs environment, especially the M4 and M4.5 membranes.

Conclusions

As a stable functional group, 1,2-dimethylimidazolium cation is suitable as the functional groups for AAEMs. Consequently, AAEMs based on 1,2-dimethylimidazolium were prepared and characterized systematically. The resultant membranes display excellent thermal stability and relatively good alkali stability. The hydroxide conductivity of the membranes is up to 20.8 mS cm⁻¹ at room temperature in deionized water, which could meet the basic requirement for the AAEMFCs. Moreover, the peak power density of the direct methanol fuel cell with the novel AAEM is 12.7 mW cm⁻² at a current density of 45 mA cm⁻², using CoO_x/C instead of Pt/C as the electrocatalyst. The results show that the 1,2-methylimidazolium functional group has the potential application for the AAEMs in AAEMFCs. Further work on improving the conductivity of the 1,2-methylimidazolium-based membranes and optimizing the electrode structure of the AAEMFCs would be carried out in detail.

Acknowledgement

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List of symbols

IEC	ion-exchange capacity, mmol g ⁻¹
N _{OHCl}	moles of HCl before titration
N _{iHCl}	moles of HCl after titration
m	the weight of dry membrane in OH ⁻ form
W _U	water uptake, wt%
W _{wet}	the weights of hydrated membranes, g
W _{dry}	the weights of dry membranes, g
SD	swelling ratio, %
L _{wet}	the lengths of hydrated membranes, cm
L _{dry}	the lengths of dry membranes, cm
L	the distance between the working electrode and reference electrode, cm
W	the width of the membranes, cm
T	the thickness of the membranes, cm
R	the resistances of the membranes, Ω
σ	ion conductivity, S cm ⁻¹

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.ijhydene.2014.12.050>.

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